

021



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10L 1/18		A1	(11) International Publication Number: WO 95/29972
			(43) International Publication Date: 9 November 1995 (09.11.95)
(21) International Application Number: PCT/US95/04920		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 21 April 1995 (21.04.95)		Published With international search report.	
(30) Priority Data: 08/236,434 2 May 1994 (02.05.94) US			
(71) Applicant: CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).			
(72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US).			
(74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).			
(54) Title: POLYALKYL HYDROXY AND AMINO AROMATIC CARBAMATES AND FUEL COMPOSITIONS CONTAINING THE SAME			
(57) Abstract			
<p>Polyalkyl hydroxy and amino aromatic carbamates having formula (I) or a fuel-soluble salt thereof; wherein X is hydroxy or amino; R₁ and R₂ are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, lower alkoxy having 1 to 6 carbon atoms, nitro, amino, N-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or N,N-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms; R₃ is hydrogen or lower alkyl having 1 to 6 carbon atoms; and R₄ is a polyalkyl group having an average molecular weight in the range of about 400 to 5,000. The polyalkyl hydroxy and amino aromatic carbamates of formula (I) are useful as fuel additives for the prevention and control of engine deposits.</p>			
<div style="text-align: center;"> <p style="text-align: right;">(I)</p> </div>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

POLYALKYL HYDROXY AND AMINO AROMATIC CARBAMATES
AND FUEL COMPOSITIONS CONTAINING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to novel hydroxy and amino aromatic compounds. More particularly, this invention relates to novel polyalkyl hydroxy and amino aromatic carbamates and their use in fuel compositions to prevent and control engine deposits.

Description of the Related Art

It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports and intake valves, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Kreuz et al., discloses a motor fuel composition comprising a mixture of hydrocarbons in the

-2-

01 gasoline boiling range containing about 0.01 to 0.25 volume
02 percent of a high molecular weight aliphatic
03 hydrocarbon-substituted phenol in which the aliphatic
04 hydrocarbon radical has an average molecular weight in the
05 range of about 500 to 3,500. This patent teaches that
06 gasoline compositions containing minor amounts of an
07 aliphatic hydrocarbon-substituted phenol not only prevent or
08 inhibit the formation of intake valve and port deposits in a
09 gasoline engine, but also enhance the performance of the
10 fuel composition in engines designed to operate at higher
11 operating temperatures with a minimum of decomposition and
12 deposit formation in the manifold of the engine.

13
14 Similarly, U.S. Patent No. 4,134,846, issued January 16,
15 1979 to Machleder et al., discloses a fuel additive
16 composition comprising a mixture of (1) the reaction product
17 of an aliphatic hydrocarbon-substituted phenol,
18 epichlorohydrin and a primary or secondary mono- or
19 polyamine, and (2) a polyalkylene phenol. This patent
20 teaches that such compositions show excellent carburetor,
21 induction system and combustion chamber detergency and, in
22 addition, provide effective rust inhibition when used in
23 hydrocarbon fuels at low concentrations.

24
25 Amino phenols are also known to function as
26 detergents/dispersants, antioxidants and anti-corrosion
27 agents when used in fuel compositions. U.S. Patent
28 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for
29 example, discloses amino phenols having at least one
30 substantially saturated hydrocarbon-based substituent of at
31 least 30 carbon atoms. The amino phenols of this patent are
32 taught to impart useful and desirable properties to
33 oil-based lubricants and normally liquid fuels.
34

-3-

01 Nitro phenols have also been employed as fuel additives.
02 For example, U.S. Patent No. 4,347,148, issued August 31,
03 1982 to K. E. Davis, discloses nitro phenols containing at
04 least one aliphatic substituent having at least about 40
05 carbon atoms. The nitro phenols of this patent are taught
06 to be useful as detergents, dispersants, antioxidants and
07 demulsifiers for lubricating oil and fuel compositions.
08
09 In addition, U.S. Patent No. 4,231,759, issued November 4,
10 1980 to Udelhofen et al., discloses a fuel additive
11 composition comprising the Mannich condensation product of
12 (1) a high molecular weight alkyl-substituted
13 hydroxyaromatic compound wherein the alkyl group has a
14 number average molecular weight of about 600 to about 3,000,
15 (2) an amine and (3) an aldehyde. This patent teaches that
16 such Mannich condensation products provide carburetor
17 cleanliness when employed alone, and intake valve
18 cleanliness when employed in combination with a hydrocarbon
19 carrier fluid.
20
21 U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz
22 et al., discloses fuel compositions containing (1) one or
23 more polybutyl or polyisobutyl alcohols wherein the
24 polybutyl or polyisobutyl group has a number average
25 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)
26 of the polybutyl or polyisobutyl alcohol, or (3) a
27 carboxylate ester of the polybutyl or polyisobutyl alcohol.
28 This patent further teaches that when the fuel composition
29 contains an ester of a polybutyl or polyisobutyl alcohol,
30 the ester-forming acid group may be derived from saturated
31 or unsaturated, aliphatic or aromatic, acyclic or cyclic
32 mono- or polycarboxylic acids.
33
34

-4-

01 U.S. Patent No. 3,285,855, issued November 15, 1966 to
02 Dexter et al., discloses alkyl esters of dialkyl
03 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the
04 ester moiety contains from 6 to 30 carbon atoms. This
05 patent teaches that such esters are useful for stabilizing
06 polypropylene and other organic material normally subject to
07 oxidative deterioration. Similar alkyl esters containing
08 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.
09 Patent No. 5,196,565, which issued March 23, 1993 to Ross.

10

11 U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet
12 et al., discloses alkyl esters of hydroxyphenyl carboxylic
13 acids wherein the ester moiety may contain up to 23 carbon
14 atoms. This patent teaches that such compounds are useful
15 as antioxidants for stabilizing emulsion-polymerized
16 polymers.

17

18 U.S. Patent No. 3,933,470, issued January 20, 1976 to Cross
19 et al., discloses esters of hydroxycarbanilic acid, wherein
20 the ester moiety is straight or branched alkyl of 1 to
21 10 carbon atoms, cycloalkyl, benzyl, chlorobenzyl,
22 methylbenzyl, phenyl, chlorophenyl, methylphenyl, alkenyl of
23 2 to 6 carbon atoms, monohaloalkenyl, alkynyl of 2 to
24 6 carbon atoms, monohaloalkynyl, and monomethoxyalkynyl.
25 This patent teaches such hydroxycarbanilic acid esters as
26 intermediates in the preparation of alkynyloxy, alkenyloxy
27 and cyanoalkoxy carbanilic acid esters, which are useful as
28 herbicides for controlling broadleaf weeds and grasses.

29

30 It has now been discovered that certain polyalkyl hydroxy
31 and amino aromatic carbamates provide excellent control of
32 engine deposits, especially intake valve deposits, when
33 employed as fuel additives in fuel compositions.

34

-5-

SUMMARY OF THE INVENTION

The present invention provides novel polyalkyl hydroxy and amino aromatic carbamates which are useful as fuel additives for the prevention and control of engine deposits, particularly intake valve deposits.

The polyalkyl hydroxy and amino aromatic carbamates of the present invention are compounds having the formula:



or a fuel-soluble salt thereof; wherein X is hydroxy or amino; R₁ and R₂ are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, lower alkoxy having 1 to 6 carbon atoms, nitro, amino, N-alkylamino wherein the alkyl group contains 1 to 6 carbon atoms, or N,N-dialkylamino wherein each alkyl group independently contains 1 to 6 carbon atoms;

R₃ is hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R₄ is a polyalkyl group having an average molecular weight in the range of about 400 to 5,000.

The present invention further provides a fuel composition comprising a major amount of hydrocarbons boiling in the

-6-

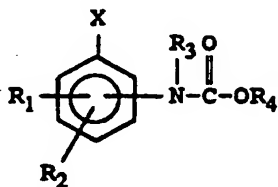
01 gasoline or diesel range and an effective
02 deposit-controlling amount of a polyalkyl hydroxy or amino
03 aromatic carbamate of the present invention.
04

05 The present invention additionally provides a fuel
06 concentrate comprising an inert stable oleophilic organic
07 solvent boiling in the range of from about 150°F to 400°F
08 and from about 10 to 70 weight percent of a polyalkyl
09 hydroxy or amino aromatic carbamate of the present
10 invention.
11

12 Among other factors, the present invention is based on the
13 surprising discovery that certain polyalkyl hydroxy and
14 amino aromatic carbamates provide excellent control of
15 engine deposits, especially on intake valves, when employed
16 as fuel additives in fuel compositions.
17

18 DETAILED DESCRIPTION OF THE INVENTION
19

20 The fuel additives provided by the present invention have
21 the general formula:
22



(I)

29
30 or a fuel-soluble salt thereof; wherein X, R₁, R₂, R₃, and R₄
31 are as defined hereinabove.
32

33 In formula I above, X can be hydroxy or amino. Preferably,
34 X is hydroxy.

-7-

01 Preferably, R_1 and R_2 are independently hydrogen, hydroxy,
02 lower alkyl of 1 to 4 carbon atoms, nitro or amino. More
03 preferably, R_1 and R_2 are independently hydrogen, hydroxy or
04 amino. Most preferably, R_1 and R_2 are independently
05 hydrogen or amino.
06

07 R_3 is preferably hydrogen or lower alkyl of 1 to 4 carbon
08 atoms. More preferably, R_3 is hydrogen, methyl or ethyl.
09

10 Preferably, R_4 is a polyalkyl group having an average
11 molecular weight in the range of about 500 to 3,000, more
12 preferably about 600 to 2,000,
13

14 When R_1 or R_2 is an N-alkylamino group, the alkyl group of
15 the N-alkylamino moiety preferably contains 1 to 4 carbon
16 atoms. More preferably, the alkyl group is methyl or ethyl.
17 For example, particularly preferred N-alkylamino groups are
18 N-methylamino and N-ethylamino groups.
19

20 Similarly, when R_1 or R_2 is an N,N-dialkylamino group, each
21 alkyl group of the N,N-dialkylamino moiety preferably
22 contains 1 to 4 carbon atoms. More preferably, each alkyl
23 group is either methyl or ethyl. For example, particularly
24 preferred N,N-dialkylamino groups are N,N-dimethylamino,
25 N-ethyl-N-methylamino and N,N-diethylamino groups.
26

27 A preferred group of polyalkyl aromatic carbamates are those
28 of formula I wherein X is hydroxy; R_1 is hydrogen, hydroxy,
29 lower alkyl of 1 to 4 carbon atoms, nitro or amino; R_2 is
30 hydrogen or amino; and R_3 is hydrogen.
31
32

33 A more preferred group of polyalkyl aromatic carbamates are
34 those of formula I wherein X is hydroxy; R_1 is hydrogen,

-8-

01 hydroxy or amino; and R_2 and R_3 are hydrogen. Even more
02 preferably, R_1 is amino and R_2 and R_3 are hydrogen.
03

04 A further preferred group of polyalkyl aromatic carbamates
05 are those of formula I wherein X is hydroxy; R_1 and R_2 are
06 amino; and R_3 is hydrogen.
07

08 It is especially preferred that the aromatic hydroxyl or
09 amino group present in the polyalkyl aromatic carbamates of
10 this invention be situated in a meta or para position
11 relative to the polyalkyl carbamate moiety. When the
12 aromatic moiety contains an additional hydroxy, nitro,
13 amino, alkylamino or dialkylamino group, it is particularly
14 preferred that the hydroxyl or amino group be in a meta or
15 para position relative to the polyalkyl carbamate moiety,
16 and in an ortho position relative to the additional hydroxy,
17 nitro, amino, alkylamino or dialkylamino group.
18

19 The polyalkyl hydroxy and amino aromatic carbamates of the
20 present invention will generally have a sufficient molecular
21 weight so as to be non-volatile at normal engine intake
22 valve operating temperatures (about 200-250°C). Typically,
23 the molecular weight of the polyalkyl hydroxy and amino
24 aromatic carbamates of this invention will range from about
25 600 to about 5,000, preferably from 600 to 3,000, more
26 preferably from 700 to 2,000.
27

28 Fuel-soluble salts of the polyalkyl hydroxy and amino
29 aromatic carbamates of the present invention are also
30 contemplated to be useful for preventing or controlling
31 deposits. For those compounds containing a hydroxy group,
32 such salts include alkali metal, alkaline earth metal,
33 ammonium, substituted ammonium and sulfonium salts.
34

-9-

01 Preferred metal salts are the alkali metal salts,
02 particularly the sodium and potassium salts, and the
03 substituted ammonium salts, particularly tetraalkyl-
04 substituted ammonium salts, such as the tetrabutylammonium
05 salts.

06
07 Fuel-soluble salts of the polyalkyl aromatic carbamates of
08 the present invention can also be readily prepared for those
09 compounds containing an amino, N-alkylamino or
10 N,N-dialkylamino group. Suitable salts include, for
11 example, those obtained by protonating the amino moiety with
12 a strong organic acid, such as an alkyl- or arylsulfonic
13 acid. Preferred salts are derived from toluenesulfonic acid
14 and methanesulfonic acid.

15

16 Definitions

17

18 As used herein, the following terms have the following
19 meanings unless expressly stated to the contrary.

20

21 The term "amino" refers to the group: $-NH_2$.

22

23 The term "N-alkylamino" refers to the group: $-NHR_a$ wherein
24 R_a is an alkyl group. The term "N,N-dialkylamino" refers to
25 the group: $-NR_bR_c$, wherein R_b and R_c are alkyl groups.

26

27 The term "alkyl" refers to both straight- and branched-chain
28 alkyl groups.

29

30 The term "lower alkyl" refers to alkyl groups having 1 to
31 about 6 carbon atoms and includes primary, secondary and
32 tertiary alkyl groups. Typical lower alkyl groups include,

33

34

-10-

01 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
02 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

03

04 The term "lower alkoxy" refers to the group $-OR_d$ wherein R_d
05 is lower alkyl. Typical lower alkoxy groups include
06 methoxy, ethoxy, and the like.

07

08 The term "polyalkyl" refers to alkyl groups which are
09 generally derived from polyolefins which are polymers or
10 copolymers of mono-olefins, particularly 1-mono-olefins,
11 such as ethylene, propylene, butylene, and the like.
12 Preferably, the mono-olefin employed will have 2 to about
13 24 carbon atoms, and more preferably, about 3 to 12 carbon
14 atoms. More preferred mono-olefins include propylene,
15 butylene, particularly isobutylene, 1-octene and 1-decene.
16 Polyolefins prepared from such mono-olefins include
17 polypropylene, polybutene, especially polyisobutene, and the
18 polyalphaolefins produced from 1-octene and 1-decene.

19

20 General Synthetic Procedures

21

22 The polyalkyl hydroxy and amino aromatic carbamates of this
23 invention may be prepared by the following general methods
24 and procedures. It should be appreciated that where typical
25 or preferred process conditions (e.g., reaction
26 temperatures, times, mole ratios of reactants, solvents,
27 pressures, etc.) are given, other process conditions may
28 also be used unless otherwise stated. Optimum reaction
29 conditions may vary with the particular reactants or
30 solvents used, but such conditions can be determined by one
31 skilled in the art by routine optimization procedures.

32

33

34

-11-

01 Moreover, those skilled in the art will recognize that it
02 may be necessary to block or protect certain functional
03 groups while conducting the following synthetic procedures.
04 In such cases, the protecting group will serve to protect
05 the functional group from undesired reactions or to block
06 its undesired reaction with other functional groups or with
07 the reagents used to carry out the desired chemical
08 transformations. The proper choice of a protecting group
09 for a particular functional group will be readily apparent
10 to one skilled in the art. Various protecting groups and
11 their introduction and removal are described, for example,
12 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*
13 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,
14 and references cited therein.

15
16 In the present synthetic procedures, a hydroxyl group will
17 preferably be protected, when necessary, as the benzyl or
18 tert-butyldimethylsilyl ether. Introduction and removal of
19 these protecting groups is well described in the art. Amino
20 groups may also require protection and this may be
21 accomplished by employing a standard amino protecting group,
22 such as a benzyloxycarbonyl or a trifluoroacetyl group.
23 Additionally, as will be discussed in further detail
24 hereinbelow, the polyalkyl aromatic carbamates of this
25 invention having an amino group on the aromatic moiety will
26 generally be prepared from the corresponding nitro
27 derivative. Accordingly, in many of the following
28 procedures, a nitro group will serve as a protecting group
29 for the amino moiety.

30
31 The polyalkyl hydroxy and amino aromatic carbamates of the
32 present invention having the formula:

33
34

-12-



07
08
09
10
11
12

wherein X, R₁, R₂, R₃ and R₄ are as defined above, may be prepared by reacting a polyalkyl alcohol having the formula:



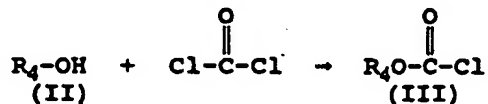
17
18
19
20
21
22

wherein R₄ is as defined above, with phosgene, COCl₂, to provide a chloroformate ester having the formula:



27
28
29
30
31
32

The above reaction may be represented as follows:



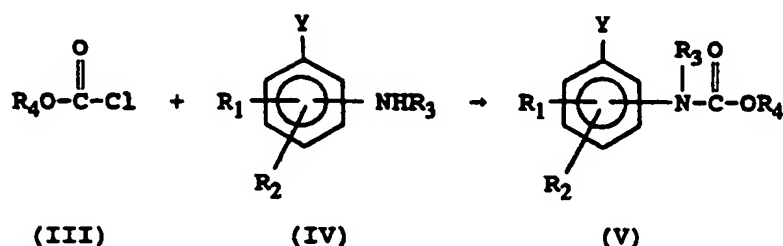
35
36
37
38
39
40

The resulting chloroformate ester of formula III is then reacted with a primary or secondary hydroxy or nitro aromatic amine having the formula:



-13-

wherein R_1 , R_2 and R_3 are as defined above, and Y is hydroxy or nitro, to provide the polyalkyl hydroxy or nitro aromatic carbamates of formula (V). This reaction may be represented as follows:



For those compounds of formula V where Y is a nitro group, reduction of the nitro group by conventional procedures will provide the desired polyalkyl amino aromatic carbamates of formula I.

The hydroxy or nitro aromatic amines of formula IV are either known compounds or can be prepared from known compounds by conventional procedures. Suitable hydroxy or nitro aromatic amines for use as starting materials in this invention include 4-aminophenol, 2-nitro-4-aminophenol, 2-nitro-5-aminophenol, 2,6-dinitro-4-aminophenol, 4-(N-methylamino)phenol, 2-nitro-4-(N-methylamino)phenol, 2-nitro-5-(N-methylamino)phenol, 2,6-dinitro-4-(N-methylamino)phenol, 2-hydroxy-4-aminophenol, 2-hydroxy-4-(N-methylamino)phenol, 2,6-dihydroxy-4-aminophenol, 2,6-dihydroxy-4-(N-methylamino)phenol, 2-t-butyl-4-aminophenol, 2-t-butyl-4-(N-methylamino)phenol, 4-nitroaniline, 3-nitroaniline, and the like.

-14-

01 Preferred hydroxy or nitro aromatic amines of formula IV
02 include 4-aminophenol, 2-nitro-4-aminophenol,
03 2-nitro-5-aminophenol, 2,6-dinitro-4-aminophenol,
04 4-nitroaniline and 3-nitroaniline.
05

06 The polyalkyl alcohols of formula II may also be prepared by
07 conventional procedures known in the art. Such procedures
08 are taught, for example, in U.S. Patent Nos. 5,055,607 to
09 Buckley and 4,859,210 to Franz et al., the disclosures of
10 which are incorporated herein by reference.
11

12 In general, the polyalkyl substituent on the polyalkyl
13 alcohols of formula II and the resulting polyalkyl hydroxy
14 and amino aromatic carbamates of the present invention will
15 have an average molecular weight in the range of about 400
16 to 5,000, preferably about 500 to 3,000, more preferably
17 about 600 to 2,000.
18

19 The polyalkyl substituent on the polyalkyl alcohols employed
20 in the invention may be generally derived from polyolefins
21 which are polymers or copolymers of mono-olefins,
22 particularly 1-mono-olefins, such as ethylene, propylene,
23 butylene, and the like. Preferably, the mono-olefin
24 employed will have 2 to about 24 carbon atoms, and more
25 preferably, about 3 to 12 carbon atoms. More preferred
26 mono-olefins include propylene, butylene, particularly
27 isobutylene, 1-octene and 1-decene. Polyolefins prepared
28 from such mono-olefins include polypropylene, polybutene,
29 especially polyisobutene, and the polyalphaolefins produced
30 from 1-octene and 1-decene.
31

32 The preferred polyisobutenes used to prepare the presently
33 employed polyalkyl alcohols are polyisobutenes which
34 comprise at least about 20% of the more reactive

-15-

01 methylvinylidene isomer, preferably at least 50% and more
02 preferably at least 70%. Suitable polyisobutenes include
03 those prepared using BF_3 catalysts. The preparation of such
04 polyisobutenes in which the methylvinylidene isomer
05 comprises a high percentage of the total composition is
06 described in U.S. Patent Nos. 4,152,499 and 4,605,808. Such
07 polyisobutenes, known as "reactive" polyisobutenes, yield
08 high molecular weight alcohols in which the hydroxyl group
09 is at or near the end of the hydrocarbon chain.
10

11 Examples of suitable polyisobutenes having a high
12 alkylvinylidene content include Ultravis 30, a polyisobutene
13 having a molecular weight of about 1300 and a
14 methylvinylidene content of about 74%, and Ultravis 10, a
15 polyisobutene having a molecular weight of about 950 and a
16 methylvinylidene content of about 76%, both available from
17 British Petroleum.
18

19 The polyalkyl alcohols may be prepared from the
20 corresponding olefins by conventional procedures. Such
21 procedures include hydration of the double bond to give an
22 alcohol. Suitable procedures for preparing such long-chain
23 alcohols are described in I. T. Harrison and S. Harrison,
24 *Compendium of Organic Synthetic Methods*, Wiley-Interscience,
25 New York (1971), pp. 119-122, as well as in U.S. Patent
26 Nos. 5,055,607 and 4,859,210.
27

28 As indicated above, the polyalkyl hydroxy and amino aromatic
29 carbamates of formula I may be prepared by first reacting a
30 polyalkyl alcohol of formula II with phosgene to form a
31 chloroformate ester.
32
33
34

-16-

01 The reaction of the polyalkyl alcohol of formula II and
02 phosgene is usually carried out on an essentially equimolar
03 basis, although excess phosgene can be used to improve the
04 degree of reaction. Any excess phosgene can be stripped
05 from the chloroformate ester product prior to reaction with
06 the hydroxy or nitro aromatic amine. The reaction is
07 typically carried out at room temperature, although
08 temperatures in the range of about -10°C to 100°C,
09 preferably about 0°C to 50°C, may be employed. The reaction
10 time will usually be in the range of about 0.5 to 48 hours.
11 The reaction may be conducted in the presence or absence of
12 an inert solvent, such as benzene, toluene, dichloromethane,
13 and the like.

14
15 The resulting chloroformate ester of formula III is then
16 reacted with a hydroxy or nitro aromatic amine of formula IV
17 to form the polyalkyl hydroxy or nitro aromatic carbamates
18 of formula V.

19
20 The reaction of chloroformate ester with the hydroxy or
21 nitro aromatic amine will generally be carried out in the
22 presence of an aprotic solvent, such as methyl cyanide, DMF,
23 acetone, chloroform, toluene or THF, containing a base
24 acceptor, such as sodium bicarbonate, sodium carbonate,
25 triethylamine or pyridine. The reaction will generally be
26 carried out at room temperature, although higher or lower
27 temperatures in the range of about -10°C to 100°C may be
28 employed.

29
30 The mole ratio of the amine nitrogen to chloroformate ester
31 will generally be in the range of about 1 to 10 moles of
32 amine nitrogen per mole of chloroformate ester. The
33 reaction time may vary from about 0.5 to about 48 hours.
34 After reaction, the desired product may be isolated by

-17-

01 conventional procedures, such as evaporation of the solvent,
02 filtration and crystallization.

03

04 Although the polyalkyl hydroxy or amino aromatic carbamates
05 of the present invention may be conveniently prepared by the
06 chloroformylation reaction described above, utilizing
07 phosgene, it is also known in the art that other methods of
08 producing carbamates are available using other reactants.
09 For example, the reaction of an isocyanate with an alcohol
10 also produces a carbamate. Accordingly, it is within the
11 skill of the art to use a selected isocyanate-substituted
12 nitro or protected hydroxyaromatic compound to react
13 directly with a polyalkyl alcohol to provide a carbamate
14 within the scope of the present invention.

15

16 When necessary, protection of the aromatic hydroxyl groups
17 on the hydroxyaromatic amines may be accomplished using
18 well-known procedures. The choice of a suitable protecting
19 group for a particular hydroxyaromatic amine will be
20 apparent to those skilled in the art. Various protecting
21 groups, and their introduction and removal, are described,
22 for example, in T. W. Greene and P. G. M. Wuts, *Protective*
23 *Groups in Organic Synthesis*, Second Edition, Wiley,
24 New York, 1991, and references cited therein.

25

26 Deprotection of the aromatic hydroxyl group(s) can also be
27 accomplished using conventional procedures. Appropriate
28 conditions for this deprotection step will depend upon the
29 protecting group(s) utilized in the synthesis and will be
30 readily apparent to those skilled in the art. For example,
31 benzyl protecting groups may be removed by hydrogenolysis
32 under 1 to about 4 atmospheres of hydrogen in the presence
33 of a catalyst, such as palladium on carbon. Typically, this
34 deprotection reaction is conducted in an inert solvent,

-18-

01 preferably a mixture of ethyl acetate and acetic acid, at a
02 temperature of from about 0°C to about 40°C for about 1 to
03 about 24 hours.

04
05 When synthesizing the polyalkyl aromatic carbamates of
06 formula I having an amino group on the aromatic moiety
07 (i.e., where X, R₁ and/or R₂ is an amino group), it is
08 generally desirable to first prepare the corresponding nitro
09 compound (i.e., where X, R₁ and/or R₂ is a nitro group) and
10 then to reduce the nitro group to an amino group using
11 conventional procedures. Aromatic nitro groups may be
12 reduced to amino groups using a number of procedures that
13 are well known in the art. For example, aromatic nitro
14 groups may be reduced under catalytic hydrogenation
15 conditions; or by using a reducing metal, such as zinc, tin,
16 iron and the like, in the presence of an acid, such as
17 dilute hydrochloric acid.

18
19 Generally, reduction of the nitro group by catalytic
20 hydrogenation is preferred. Typically, this reaction is
21 conducted using about 1 to 4 atmospheres of hydrogen and a
22 platinum or palladium catalyst, such as palladium on carbon.
23 The reaction is typically carried out at a temperature of
24 about 0°C to about 100°C for about 1 to 24 hours in an inert
25 solvent, such as ethanol, ethyl acetate and the like.
26 Hydrogenation of aromatic nitro groups is discussed in
27 further detail in, for example, P. N. Rylander, *Catalytic*
28 *Hydrogenation in Organic Synthesis*, pp. 113-137, Academic
29 Press (1979); and *Organic Synthesis, Collective Vol. I*,
30 Second Edition, pp. 240-241, John Wiley & Sons, Inc. (1941);
31 and references cited therein.

32
33
34

-19-

Fuel Compositions

01

02

03 The polyalkyl hydroxy and amino aromatic carbamates of the
04 present invention are useful as additives in hydrocarbon
05 fuels to prevent and control engine deposits, particularly
06 intake valve deposits. The proper concentration of additive
07 necessary to achieve the desired deposit control varies
08 depending upon the type of fuel employed, the type of
09 engine, and the presence of other fuel additives.

10

11 In general, the concentration of the polyalkyl aromatic
12 carbamates of this invention in hydrocarbon fuel will range
13 from about 50 to about 2500 parts per million (ppm) by
14 weight, preferably from 75 to 1,000 ppm. When other deposit
15 control additives are present, a lesser amount of the
16 present additive may be used.

17

18 The polyalkyl aromatic carbamates of the present invention
19 may be formulated as a concentrate using an inert stable
20 oleophilic (i.e., dissolves in gasoline) organic solvent
21 boiling in the range of about 150°F to 400°F (about 65°C to
22 205°C). Preferably, an aliphatic or an aromatic hydrocarbon
23 solvent is used, such as benzene, toluene, xylene or
24 higher-boiling aromatics or aromatic thinners. Aliphatic
25 alcohols containing about 3 to 8 carbon atoms, such as
26 isopropanol, isobutylcarbinol, n-butanol and the like, in
27 combination with hydrocarbon solvents are also suitable for
28 use with the present additives. In the concentrate, the
29 amount of the additive will generally range from about 10 to
30 about 70 weight percent, preferably 10 to 50 weight percent,
31 more preferably from 20 to 40 weight percent.

32

33 In gasoline fuels, other fuel additives may be employed with
34 the additives of the present invention, including, for

-20-

01 example, oxygenates, such as t-butyl methyl ether, antiknock
02 agents, such as methylcyclopentadienyl manganese
03 tricarbonyl, and other dispersants/detergents, such as
04 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or
05 succinimides. Additionally, antioxidants, metal
06 deactivators and demulsifiers may be present.

07

08 In diesel fuels, other well-known additives can be employed,
09 such as pour point depressants, flow improvers, cetane
10 improvers, and the like.

11

12 A fuel-soluble, nonvolatile carrier fluid or oil may also be
13 used with the polyalkyl aromatic carbamates of this
14 invention. The carrier fluid is a chemically inert
15 hydrocarbon-soluble liquid vehicle which substantially
16 increases the nonvolatile residue (NVR), or solvent-free
17 liquid fraction of the fuel additive composition while not
18 overwhelmingly contributing to octane requirement increase.
19 The carrier fluid may be a natural or synthetic oil, such as
20 mineral oil, refined petroleum oils, synthetic polyalkanes
21 and alkenes, including hydrogenated and unhydrogenated
22 polyalphaolefins, and synthetic polyoxyalkylene-derived
23 oils, such as those described, for example, in U.S. Patent
24 No. 4,191,537 to Lewis, and polyesters, such as those
25 described, for example, in U.S. Patent Nos. 3,756,793 and
26 5,004,478 to Robinson and Vogel et al., respectively, and in
27 European Patent Application Nos. 356,726 and 382,159,
28 published March 7, 1990 and August 16, 1990, respectively.

29

30 These carrier fluids are believed to act as a carrier for
31 the fuel additives of the present invention and to assist in
32 removing and retarding deposits. The carrier fluid may also
33 exhibit synergistic deposit control properties when used in

34

-21-

01 combination with a polyalkyl aromatic carbamate compound of
02 this invention.

03

04 The carrier fluids are typically employed in amounts ranging
05 from about 100 to about 5000 ppm by weight of the
06 hydrocarbon fuel, preferably from 400 to 3000 ppm of the
07 fuel. Preferably, the ratio of carrier fluid to deposit
08 control additive will range from about 0.5:1 to about 10:1,
09 more preferably from 1:1 to 4:1, most preferably about 2:1.

10

11 When employed in a fuel concentrate, carrier fluids will
12 generally be present in amounts ranging from about 20 to
13 about 60 weight percent, preferably from 30 to 50 weight
14 percent.

15

16

EXAMPLES

17

18 The following examples are presented to illustrate specific
19 embodiments of the present invention and synthetic
20 preparations thereof; and should not be interpreted as
21 limitations upon the scope of the invention.

22

23

Example 1

24

25

Preparation of Polyisobutylchloroformate

26

27 Toluene (100 mL) and phosgene (130 mL of a 20 weight percent
28 solution dissolved in toluene) were cooled to 0°C under
29 nitrogen. Polyisobutanol (50.0 grams, molecular weight
30 average 984, prepared via hydroformylation of Amoco H-100
31 polyisobutene) dissolved in toluene (100 mL) was added
32 dropwise. The cooling bath was removed and the reaction was
33 stirred at room temperature for six hours. The solvent was

34

-22-

01 removed in vacuo to yield 39.5 grams of the desired
02 chloroformate as a light yellow oil.

03

04

Example 2

05

06

Preparation of

07

Polyisobutyl-N-4-hydroxy-3-nitrophenylcarbamate

08

09 A solution of 39.5 grams of the product from Example 1 in
10 chloroform (500 mL, filtered through activity 1 basic
11 alumina) containing 4.54 grams of sodium bicarbonate and
12 8.32 grams of 4-hydroxy-3-nitroaniline was refluxed for
13 sixteen hours under nitrogen. The mixture was cooled to
14 room temperature, diluted with dichloromethane (1.2 L) and
15 washed once with saturated aqueous sodium bicarbonate
16 solution, twice with water and once with saturated aqueous
17 sodium chloride. The organic layer was dried over anhydrous
18 magnesium sulfate, filtered and concentrated in vacuo to
19 yield 49.5 grams of a yellow brown oil. The oil was
20 chromatographed on silica gel eluting with hexane followed
21 by hexane/ethylacetate/ethanol (9:0.8:0.2) to yield
22 34.1 grams of the desired product as an orange oil. IR
23 (neat) 1736, 1708 cm^{-1} . ^1H NMR (CDCl_3) δ 10.4 (s, 1H), 8.2
24 (bs, 1H), 7.7 (d, 1H), 7.15 (d, 1H), 6.7 (bs, 1H), 4.2 (t,
25 2H), 0.6-1.8 (m, 137H).

26

27

28

29

30

31

32

33

34

-23-

Example 3

Preparation of

Polyisobutyl-N-4-hydroxy-3-aminophenylcarbamate

A solution of 22.1 grams of the product from Example 2 in 200 mL of ethylacetate containing 3.0 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for sixteen hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yielded 14.7 grams of the desired product as a brown oil. ¹H NMR (CDCl₃) δ 6.9 (bs, 1H), 6.65 (d, 1H), 6.5 (d, 1H), 6.35 (bs, 1H), 4.15 (t, 2H), 4.0 (bs, 3H), 0.6-1.8 (m, 137H).

Example 4

Preparation of

Polyisobutyl-N-4-hydroxyphenylcarbamate

A solution of 19.2 grams of the product prepared as in Example 1 in toluene (150 mL) containing 2.73 grams of 4-hydroxyaniline and 3.8 mL of triethylamine was refluxed for sixteen hours under nitrogen. The mixture was cooled to room temperature, diluted with hexane (450 mL) and washed once with water, once with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 27.1 grams of a brown oil. The oil was chromatographed on silica gel eluting with hexane followed by hexane/ethylacetate/ethanol (96:2:2) to yield 11.1 grams of the desired product as a yellow oil. ¹H NMR (CDCl₃) δ

-24-

01 7.4 (d, 2H), 7.15 (d, 2H), 6.6 (bs, 1H), 4.2 (t, 2H),
02 0.6-1.8 (m, 137H).

03

04

Example 5

05

06

Single-Cylinder Engine Test

07

08 The test compounds were blended in gasoline and their
09 deposit reducing capacity determined in an ASTM/CFR
10 single-cylinder engine test.

11

12 A Waukesha CFR single-cylinder engine was used. Each run
13 was carried out for 15 hours, at the end of which time the
14 intake valve was removed, washed with hexane and weighed.
15 The previously determined weight of the clean valve was
16 subtracted from the weight of the valve at the end of the
17 run. The differences between the two weights is the weight
18 of the deposit. A lesser amount of deposit indicates a
19 superior additive. The operating conditions of the test
20 were as follows: water jacket temperature 200°F; vacuum of
21 12 in Hg, air-fuel ratio of 12, ignition spark timing of
22 40° BTC; engine speed is 1800 rpm; the crankcase oil is a
23 commercial 30W oil.

24

25 The amount of carbonaceous deposit in milligrams on the
26 intake valves is reported for each of the test compounds in
27 Table I and Table II.

28

29

30

31

32

33

34

-25-

TABLE I

Intake Valve Deposit Weight
(in milligrams)

Sample ¹	Run 1	Run 2	Average
Base Fuel	253.4	235.5	244.5
Example 2	30.1	23.2	26.7
Example 3	9.9	7.2	8.6

¹At 150 parts per million actives (ppma).

TABLE II

Intake Valve Deposit Weight
(in milligrams)

Sample ¹	Run 1	Run 2	Average
Base Fuel	302.6	300.4	301.5
Example 4	5.7	4.5	5.1

¹At 200 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give concentrations of 150 and 200 ppma (parts per million actives), as indicated in the tables.

The data in Table I and Table II illustrates the significant reduction in intake valve deposits provided by the polyalkyl aromatic carbamates of the present invention (Examples 2, 3 and 4) compared to the base fuel.

-26-

01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

05

06

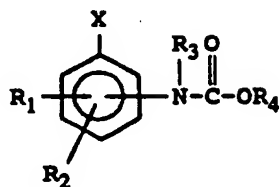
07

08

09

10

11



12 or a fuel-soluble salt thereof; wherein

13

14 X is hydroxy or amino;

15

16 R₁ and R₂ are independently hydrogen, hydroxy, lower
17 alkyl having 1 to 6 carbon atoms, lower alkoxy having 1
18 to 6 carbon atoms, nitro, amino, N-alkylamino wherein
19 the alkyl group contains 1 to 6 carbon atoms, or
20 N,N-dialkylamino wherein each alkyl group independently
21 contains 1 to 6 carbon atoms;

22

23 R₃ is hydrogen or lower alkyl having 1 to 6 carbon
24 atoms; and

25

26 R₄ is a polyalkyl group having an average molecular
27 weight in the range of about 400 to 5,000.

28

29 2. The compound according to Claim 1, wherein R₁ and R₂
30 are independently hydrogen, hydroxy, lower alkyl of 1
31 to 4 carbon atoms, nitro or amino; and X is hydroxy.

32

33

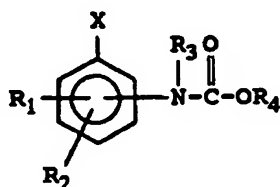
34

-27-

- 01 3. The compound according to Claim 2, wherein R_1 and R_2
02 are independently hydrogen, hydroxy or amino.
03
- 04 4. The compound according to Claim 3, wherein R_1 and R_2
05 are independently hydrogen or amino.
06
- 07 5. The compound according to Claim 4, wherein R_1 is amino
08 and R_2 is hydrogen.
09
- 10 6. The compound according to Claim 4, wherein R_1 and R_2
11 are both amino.
12
- 13 7. The compound according to Claim 1, wherein R_3 is
14 hydrogen or lower alkyl of 1 to 4 carbon atoms.
15
- 16 8. The compound according to Claim 1, wherein R_4 is a
17 polyalkyl group having an average molecular weight in
18 the range of about 500 to 3,000.
19
- 20 9. The compound according to Claim 8, wherein R_4 has an
21 average molecular weight in the range of about 600 to
22 2,000.
23
- 24 10. The compound according to Claim 1, wherein R_4 is a
25 polyalkyl group derived from polypropylene, polybutene,
26 or polyalphaolefin oligomers of 1-octene or 1-decene.
27
- 28 11. The compound according to Claim 10, wherein R_4 is
29 derived from polyisobutene.
30
- 31 12. The compound according to Claim 11, wherein the
32 polyisobutene contains at least about 20% of a
33 methylvinylidene isomer.
34

-28-

- 01 13. A fuel composition comprising a major amount of
02 hydrocarbons boiling in the gasoline or diesel range
03 and an effective detergent amount of a compound of the
04 formula:
05



13 or a fuel-soluble salt thereof; wherein

14
15 X is hydroxy or amino;

16
17 R₁ and R₂ are independently hydrogen, hydroxy, lower
18 alkyl having 1 to 6 carbon atoms, lower alkoxy having 1
19 to 6 carbon atoms, nitro, amino, N-alkylamino wherein
20 the alkyl group contains 1 to 6 carbon atoms, or
21 N,N-dialkylamino wherein each alkyl group independently
22 contains 1 to 6 carbon atoms;

23
24 R₃ is hydrogen or lower alkyl having 1 to 6 carbon
25 atoms; and

26
27 R₄ is a polyalkyl group having an average molecular
28 weight in the range of about 400 to 5,000.
29

- 30 14. The fuel composition according to Claim 13, wherein R₁
31 and R₂ are independently hydrogen, hydroxy, lower alkyl
32 of 1 to 4 carbon atoms, nitro or amino; and X is
33 hydroxy.
34

-29-

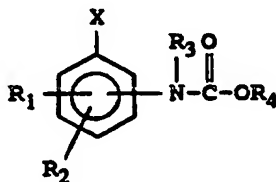
- 01 15. The fuel composition according to Claim 14, wherein R_1
02 and R_2 are independently hydrogen, hydroxy or amino.
03
- 04 16. The fuel composition according to Claim 15, wherein R_1
05 and R_2 are independently hydrogen or amino.
06
- 07 17. The fuel composition according to Claim 16, wherein R_1
08 is amino and R_2 is hydrogen.
09
- 10 18. The fuel composition according to Claim 16, wherein R_1
11 and R_2 are both amino.
12
- 13 19. The fuel composition according to Claim 13, wherein R_3
14 is hydrogen or lower alkyl of 1 to 4 carbon atoms.
15
- 16 20. The fuel composition according to Claim 13, wherein R_4
17 is a polyalkyl group having an average molecular weight
18 in the range of about 500 to 3,000.
19
- 20 21. The fuel composition according to Claim 20, wherein R_4
22 has an average molecular weight in the range of about
23 600 to 2,000.
24
- 25 22. The fuel composition according to Claim 13, wherein R_4
26 is a polyalkyl group derived from polypropylene,
27 polybutene, or polyalphaolefin oligomers of 1-octene or
28 1-decene.
29
- 30 23. The fuel composition according to Claim 22, wherein R_4
31 is derived from polyisobutene.
32
33
34

-30-

01 24. The fuel composition according to Claim 23, wherein the
02 polyisobutene contains at least about 20% of a
03 methylvinylidene isomer.
04

05 25. The fuel composition according to Claim 13, wherein
06 said composition contains about 50 to about 2500 parts
07 per million by weight of said compound.
08

09 26. A fuel concentrate comprising an inert stable
10 oleophilic organic solvent boiling in the range of from
11 about 150°F to 400°F and from about 10 to about
12 70 weight percent of a compound of the formula:
13



21 or a fuel-soluble salt thereof; wherein

22
23 X is hydroxy or amino;

24
25 R₁ and R₂ are independently hydrogen, hydroxy, lower
26 alkyl having 1 to 6 carbon atoms, lower alkoxy having 1
27 to 6 carbon atoms, nitro, amino, N-alkylamino wherein
28 the alkyl group contains 1 to 6 carbon atoms, or
29 N,N-dialkylamino wherein each alkyl group independently
30 contains 1 to 6 carbon atoms;

31
32 R₃ is hydrogen or lower alkyl having 1 to 6 carbon
33 atoms; and
34

-31-

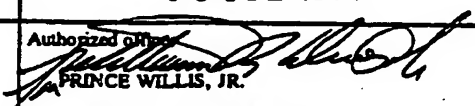
- 01 R_4 is a polyalkyl group having an average molecular
02 weight in the range of about 400 to 5,000.
03
- 04 27. The fuel concentrate according to Claim 26, wherein R_1
05 and R_2 are independently hydrogen, hydroxy, lower alkyl
06 of 1 to 4 carbon atoms, nitro or amino; and X is
07 hydroxy.
08
- 09 28. The fuel concentrate according to Claim 27, wherein R_1
10 and R_2 are independently hydrogen, hydroxy or amino.
11
- 12 29. The fuel concentrate according to Claim 28, wherein R_1
13 and R_2 are independently hydrogen or amino.
14
- 15 30. The fuel concentrate according to Claim 29, wherein R_1
16 is amino and R_2 is hydrogen.
17
- 18 31. The fuel concentrate according to Claim 29, wherein R_1
19 and R_2 are both amino.
20
- 21
- 22 32. The fuel concentrate according to Claim 26, wherein R_3
23 is hydrogen or lower alkyl of 1 to 4 carbon atoms.
24
- 25 33. The fuel concentrate according to Claim 26, wherein R_4
26 is a polyalkyl group having an average molecular weight
27 in the range of about 500 to 3,000.
28
- 29 34. The fuel concentrate according to Claim 33, wherein R_4
30 has an average molecular weight in the range of about
31 600 to 2,000.
32
33
34

-32-

- 01 35. The fuel concentrate according to Claim 26, wherein R_4
02 is a polyalkyl group derived from polypropylene,
03 polybutene, or polyalphaolefin oligomers of 1-octene or
04 1-decene.
05
- 06 36. The fuel concentrate according to Claim 35, wherein R_4
07 is derived from polyisobutene.
08
- 09 37. The fuel concentrate according to Claim 36, wherein the
10 polyisobutene contains at least about 20% of a
11 methylvinylidene isomer.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/04920

A. CLASSIFICATION OF SUBJECT MATTER				
IPC(6) : C10L 1/18 US CL : 44/387, 408, 418, 426, 428; 560/24, 132 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) U.S. : 44/387, 408, 418, 426, 428; 560/24, 132				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
A	US, A, 4,550,188 (FRULLA ET AL) 29 October 1985, see entire document.	1-12		
A	US, A, 4,748,265 (OXBOL ET AL) 31 May 1988, see entire document.	1-12		
A	US, A, 5,246,912 (NIELSEN) 21 September 1993, see entire document.	1-12		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.				
<table border="0"> <tr> <td style="vertical-align: top;"> <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understate the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understate the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understate the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>			
Date of the actual completion of the international search 05 JUNE 1995		Date of mailing of the international search report 03 JUL 1995		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer  PRINCE WILLIS, JR. Telephone No. (703) 308-0661		